Comparison of Water Uptake as Function of Surface Modification of Empty Fruit Bunch Oil Palm Fibres in PP Biocomposites

Thorsak Kittikorn,[a] Emma Strömberg,[a] Monica Ek,[a] and Sigbritt Karlsson [a,b,]*

Empty fruit bunch oil palm (EFBOP) fibres were surface modified by four different methods, propionylation, vinyltrimethoxy silanization, PPgMA dissolution modification, and PPgMA blending, and integrated into a polypropylene (PP) matrix. The designed biocomposites were subjected to an absorption process at different temperatures. Their water uptake behaviour was compared with the unmodified fibre biocomposites. An increased fibre content and temperature resulted in increased water uptake for all of the biocomposites. The biocomposites containing modified fibres showed a reduction in water uptake, rate of diffusion, sorption, and permeation in comparison with unmodified fibre composites. Comparing the 20 wt% fibre composites at ambient temperature, the performance in water absorption followed the sequence silanization < propionylation < PPgMA dissolution modification < PPgMA blending < no modification. Furthermore, the lowest water absorption was obtained from the silanized fibre/PP composite with 40% fibre content at ambient temperature. Dissolution or blending of PPgMA gave similar water uptake results. The reduction of diffusion, sorption, and permeation confirmed that the modification of fibres was potentially effective at resisting water penetration into the composites.

Keywords: Oil palm fibre; Polypropylene; Biocomposite; Fibre modification; Water

*Contact information: a: Department of Fibre and Polymer Technology, School of Chemical Science and Engineering, KTH Royal Institute of Technology, SE-100 44 STOCKHOLM, Sweden; b: University of Skövde, SKÖVDE, Sweden; * Corresponding author: sigbritt@kth.se*

INTRODUCTION

Sustainable lignocellulosic fibre/polymer composites are good candidates for a renewable resource alternative to conventional plastic composites (such as glass fibre composites, *etc*.). Presently, there is enormous development and commercialization in many fields of applications such as construction, household equipment, packaging, and automobile industries. In general, the incorporation of the cellulose fibre into composites has advantages, *e.g*., decrease in weight, reduction of product cost, and improvement of mechanical properties that depend on fibre-matrix phase adhesion (Vilaplana *et al.* 2010; Summerscales *et al.* 2010; Hill 2006; Bledzki and Gassan 1999).

Empty fruit bunch oil palm fibre (EFBOP fibre) is a natural material that has the potential to be used in composites (Law *et al.* 2007). In Southeast Asia, and particularly Thailand, the oil palm plant has been promoted for the past decade due to its versatility. In general, the EFBOP fibre is obtained as residual waste in a by-product of the oil palm biorefinery process. Each ton of palm oil produces more than a ton of EFBOP, and its waste management causes serious adverse environmental impacts, since the material is incinerated, with a resulting emission of CO_2 into the environment. The use of these residues as reinforcement fibres in composites could be a suitable approach to give added value to these wastes.

The incorporation of cellulose or lignocellulosic fibres into conventional polymers such as polyolefins results in difficulties in homogenization and low performance in mechanical properties due to poor compatibility between fibre and the matrix. Furthermore, higher water uptake in composites directly results in a reduction of the service life. Therefore, any development of new biocomposites should include a study of water absorption to define a sustainable reinforcement system and validate its suitability for application in composites. In water uptake, water (or moisture) is transportable in the composite by hydroxyl groups of cellulose. Water diffuses from the matrix through the fibre *via* the interface boundary. The molecules of water are absorbed in the fibre or voids at the boundary in materials due to the affinity of the water-cellulose interaction. This causes swelling and hydrolysis degradation in the materials. However, the shrinkage of composites would occur after moisture removal and result in stress cracking (Kobiki and Kawada 2005). Furthermore, moisture in biocomposites also increases the risk of microbial degradation by offering a suitable surface for the colonisation of microorganisms, resulting in biofilm formation (Strömberg and Karlsson 2009). In order to prevent water uptake in cellulose fibre/plastic composites, surface modifications of fibres can be used to improve the hydrophobicity of cellulose and to enhance interfacial adhesion, ultimately increasing the adhesion between the polymer matrix and the fibre.

Chemical or physical methods can be used to improve the hydrophobic property of cellulose, allowing increased interfacial adhesion between matrix and fibre. By chemically functionalizing with hydrophobic substituents, the adhesion of the hydroxyl groups of cellulose is improved and the susceptibility to water may be decreased (Shinoj *et al.* 2011; La Mantia and Morreale 2011). There are many chemical surface treatments applicable to lignocellulosic fibres, *e.g*., alkaline treatment, peroxide treatment, latex treatment, acetylation, propionylation, benzoylation, silanization, and isocyanate (Bledzki and Gassan 1999; Sreekala and Thomas 2003; Abdelmouleha *et al.* 2004). Silane treatment imparts a coating on the fibre surface (Xie *et al*. 2010), but esterification (such as acetylation or propionylation) directly improves the hydrophobic property of the fibre (Tserki *et al.* 2005). Alkaline treatment, on the other hand, results in a rough surface by making pores wider on the fibre. Using chemical treatments on the fibres prior to compounding is, in general, more complex and expensive (La Matia and Morreale 2011). Therefore, the use of compatibilizers as the third components in compounding processes is the most popular method, because it results in efficiency similar to chemical treatments but avoids the pretreatment step, which is expensive.

Earlier work presented the thermo-mechanical properties of biocomposites made by compatibilization of cellulose fibres obtained from recycled papers and PP matrix using different methods (Espert *et al.* 2003). The methods involved blending, preblending, silanization, and acetylation of cellulose, which resulted in improved thermal and thermo-oxidative stability (Espert *et al.* 2003). The water absorption in these biocomposites was studied by immersing the composites in water at three different temperatures: 23, 50, and 70 °C. The process of absorption of water was found to follow the kinetics and mechanisms described by Fick's theory (Espert *et al.* 2004). A kinetic study of water absorption in biocomposites demonstrated that fibre modification could decrease the rate of diffusion, sorption, and permeation (Espert *et al.* 2004). Furthermore, increased temperatures resulted in an increase in water uptake (Najafi *et al*. 2007) as the rate of diffusion in the composites as well.

The objective of the present work was to compare the water uptake in biocomposites made from polypropylene (PP) and EFBOP fibres. In an effort to reduce water uptake in the composites, the EFBOP fibres were modified using the reagents propionic anhydride (Tserki *et al.* 2005), vinyltrimethoxysilane (Espert *et al.* 2003; Sreekala *et al.* 1997; Sreekala *et al.* 1997; Sreekumar *et al.* 2009), and maleic anhydride grafted polypropylene (PPgMA) hot solution (Espert *et al.* 2003). PPgMA granules were also exploited as the compatibilizer during the compounding process (Gonzalez-Sanchez *et al.* 2008; Rozman *et al.* 1998; Abu Sharkh *et al.* 2004) to substitute the OH groups of cellulose. Due to inherent hydrophobicity of those functional groups, the treatment enhanced the hydrophobicity of the fibre and also improved interfacial adhesion between the two constituents. For comparison, PP biocomposite was also manufactured using a compatibilizer as the third component during melt-blending. The biofibres and PP were mixed together with fibre contents of 5%, 10%, 20%, and 40% w/w using an internal mixer (Brabender) without a free radical-promoting catalyst. A compression moulding technique was used to produce composite sheets. SEM was used to monitor the surface morphology.

EXPERIMENTAL

Materials

Empty fruit bunch oil palm (EFBOP) fibre was kindly supplied by the Nam Hong Palm Company in Thailand. Generally, EFBOP fibre consists of cellulose (62.9%), hemicelluloses (18%), lignin (17.8%), and ash (1.3%). Its tensile strength and modulus are 71 MPa and 1.7 GPa, respectively (Sreekala *et al.* 1997). Polypropylene grade HE125MO (MFI 12 g/10 min) was supplied by Borealis. Sodium hydroxide, propionic anhydride (Fluka, 96%), maleic anhydride grafted polypropylene (PPgMA) (Sigma Aldrich, Mw = 9100), and vinyltrimethoxysilane (Sigma Aldrich, 98%, density 0.971 g/cm^3) were used as reagents for chemical modification. Toluene (Sigma Aldrich, 99.9%), ethanol (96%), and acetone (commercial grade) were used as solvents in the chemical modification processes.

Methods

Fibre preparation

Empty fruit bunch oil palm (EFBOP) fibre was washed in water several times to get rid of contaminants on the fibre and then dried in a ventilated oven at 70 °C. Afterward, it was cut to short length, roughly 30 to 40 mm.

Alkaline treatment

The EFBOP fibre was immersed in 6% w/w NaOH solution at room temperature for 48 h to remove non-cellulose compounds such as wax or hemicelluloses. After 48 h, the fibres were washed in water until the pH was neutral and then dried in a ventilated oven at 70 °C for 24 h.

Chemical modification of fibres: Propionylation

The alkaline-treated fibres were put in a 250 mL flask and then rinsed with propionic anhydride to ensure that the fibres were completely covered. The procedure followed a previous study (Tserki *et al.* 2005). The flask was placed in the oven, and an esterification was carried out at 140 °C for 2 h. After that, the esterified fibres were washed with acetone and water to remove any propionic anhydride residue.

PPgMA modification

PPgMA pellets were dissolved in 200 mL of toluene, contained in a one-neck round bottom flask at 120 °C under reflux conditions. The alkaline-treated fibres were added to the solution, in a weight ratio of PPgMA to fibre of 5%. The reaction took place at 130 to 135 °C under reflux conditions for 2 h. After that, the fibres were washed in water and dried in a ventilated oven at 70 °C. To remove PPgMA residue, the modified fibres were further extracted in a reflux process by toluene for 3 h.

Vinyltrimethoxysilane treatment

Two grams of vinyltrimethoxysilane were added to 100 mL of a solvent mixture of 60% ethanol/40% water (v/v) and stirred for 1 h. Thereafter, the pH was adjusted by adding acetic acid to obtain pH 4, and then further stirred for 15 min. At the same time, the fibres were immersed in NaOH solution (1% w/w) for 1 h and then neutralized by water and soaked. Five grams of fibres were added to the vinyltrimethoxysilane solution and stirred with a magnetic bar. The reaction took place for 2 h at 25 °C. The silane-treated fibres were thereafter dried in a ventilated oven at 60 °C for 24 h.

Composite Preparation

The fibres were milled by a grinding machine. The dimension of the fibres was 3.5±1.3 mm (length) and 310±90 μm (width) (Fig. 1). The fibres were thereafter compounded with PP in a Brabender internal mixing machine. Fibre/PP composites of fibre contents 5, 10, 20, and 40% w/w were prepared. The Brabender zone temperature was set up at 200, 190, and 200 °C with a rotation speed of 40 rpm. PP was initially added in the Brabender to melt at a slow speed of 25 rpm. Subsequently, the chopped fibres were mixed with the molten PP for a holding time of 5 min. The same procedure was conducted for preparation of the blend with PPgMA and unmodified fibres. After compounding, the composites were ground by a grinding machine to obtain pellets for the next processing step.

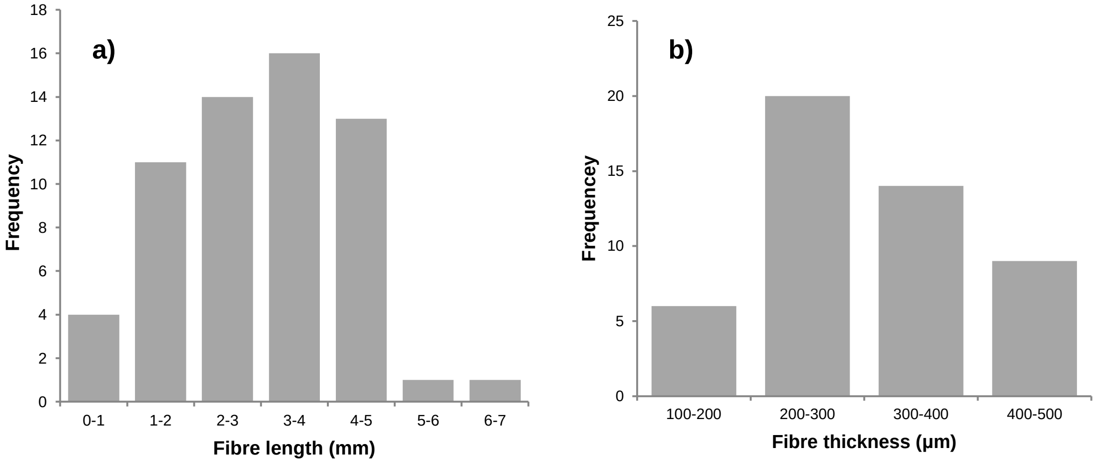


Fig. 1. a) Fibre length distribution and **b)** fibre thickness distribution

Composite sheets of dimensions 150 × 70 × 2 mm^3 were prepared *via* a compression moulding process. The temperature of the upper and lower plate was 170 °C under a pressing force of 5 tonnes for 5 min. The plates were left to cool down in ambient temperature.

Fibre dimension distribution

The fibres were extracted from PP composites by toluene reflux at 110 °C for 4 h. Afterward, the fibres were kept in desiccators 48 h for moisture removal. In order to measure the distribution of fibre length and thickness, the fibres were measured by exploiting a calliper gauge and SEM analysis, respectively.

Characterization

Surface morphology image

A Hitachi model S-4800 scanning electron microscope was used for analysis. The samples were cut into small pieces and dried at 70 °C for 24 h and then kept in a desiccator for 48 h. The surfaces of fibres and cross-sections of fractured (by tensile test) biocomposite samples were analysed to estimate the surface morphology of the fibres and the interface between the fibres and PP matrix. The specimens were coated by gold-palladium sputtering before SEM analysis.

Water uptake studies

The water absorption test was carried out in accordance with ASTM 570 (Espert *et al.* 2004). The composite sheets were cut to specimen dimensions of 30 × 5 × 2 mm^3. The thickness of samples was 2±0.05 mm. The samples were dried to evaporate moisture from the composite at 70 °C for 24 h and further kept in a desiccator for 48 h. The weight of the dried specimen was measured and recorded. Six samples were placed in a bottle tank containing deionized water and placed in an oven at temperatures of 25, 50, and 70 °C. The weight of the samples was measured and recorded at regular intervals after the water on the surface of the samples was dried by wiping with paper. The water absorption (%) was calculated using the following equation,

$$\text{Mt}\ (\%) = \left(\frac{w_t - w_0}{w_0}\right) \times 100 \tag{1}$$

where w_t is weight of the sample at each time and w_0 is the initial weight of the sample.

The kinetic parameters of water sorption could be determined using a linear regression analysis of Equation 2,

$$\log\left(\frac{M_t}{M_\infty}\right) = \log k + n \log t \tag{2}$$

where M_∞ is the mass of absorbed water at infinite time (equilibrium), M_t is the mass of water absorbed at interval time, k is a constant parameter, n is a kinetic parameter, and t is the time of exposure.

The diffusivity, sorption, and permeation were studied using the Fickian model. The diffusion coefficient, D, was calculated by the following correlation,

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{D}{\pi}\right)^{0.5} t^{0.5} \tag{3}$$

where *D* is the diffusion coefficient, and *L* is the thickness of the sample. The sorption coefficient, *S,* is calculated by Equation 4,

$$S = \frac{M_\infty}{M_0} \tag{4}$$

where M_∞ is the mass of absorbed water at infinite time (equilibrium), and M_0 is the initial mass of the sample. The permeation coefficient can be calculated by Equation 5,

$$P = D \times S \tag{5}$$

where *D* and *S* are the diffusion and sorption coefficients, respectively.

RESULTS AND DISCUSSION

Water Absorption Analysis

Figure 2 presents water absorption curves for unmodified fibre PP composites at 23 °C. It demonstrates that the absorbed water increased with fibre content in unmodified fibre PP composites and reached a maximum at 40% fibre content. Similar behaviour was observed for the modified fibre PP composites at the absorption temperatures of 50 °C and 70 °C. These results are summarized in Table 1. This indicated that the water uptake capability in a composite is dependent on the amount of cellulose fibre it contains, due to the affinity of hydroxyl groups of cellulose for water.

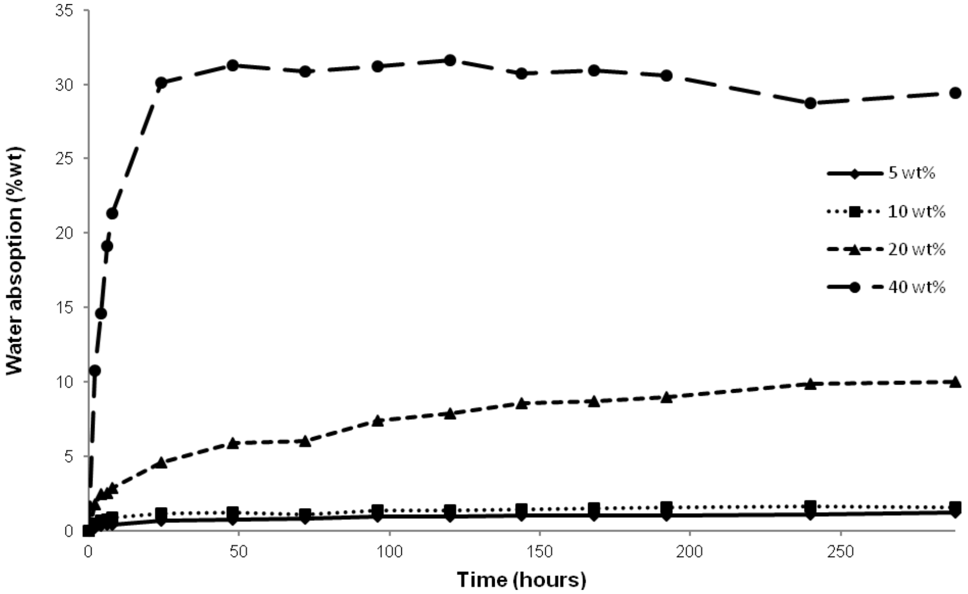


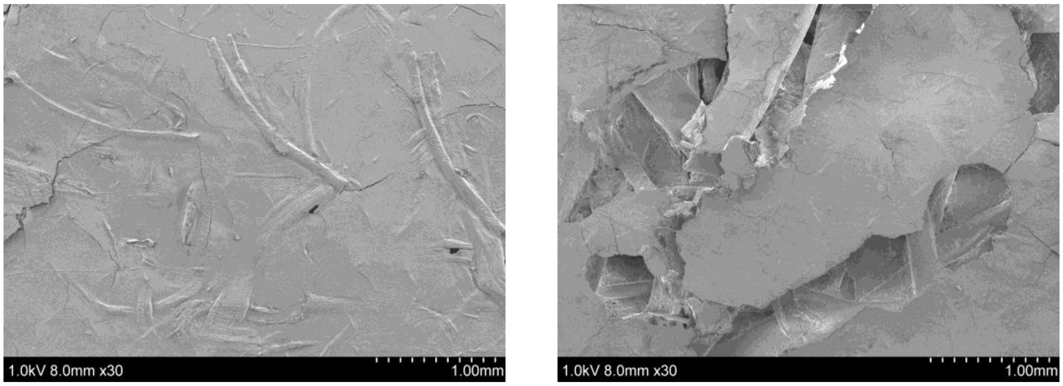
Fig. 2. Water absorption behaviour of EFBOP fibre PP composite with varying fibre content at 23 °C

Table 1. Water Absorption of Each Fibre PP Composite at Various Fibre Contents and Temperatures

Fibre PP composite	Fibre content (wt%)	Water absorption %, (Saturation time, hours)		
		23 °C	50 °C	70 °C
Unmodified fibre	5	1.2 (96)	1.4 (96)	1.5 (96)
	10	1.6 (96)	2.4 (96)	3.0 (96)
	20	9.9 (144)	14.5 (96)	13.1 (96)
	40	29.0 (48)	30.6 (24)	28.7 (24)
PPgMA blend fibre	5	0.7 (120)	1.0 (72)	1.2 (48)
	10	1.3 (144)	2.7 (144)	3.4 (96)
	20	5.1 (144)	6.3 (96)	9.7 (96)
	40	26.2 (120)	23.4 (96)	27.2 (96)
PPgMA modified fibre	5	0.7 (120)	0.9 (120)	1.2 (120)
	10	1.9 (120)	2.7 (120)	3.3 (120)
	20	4.7 (144)	6.9 (144)	6.7 (72)
	40	28.2 (96)	27.1 (96)	22.7 (96)
Propionylated fibre	5	0.7 (72)	1.2 (96)	1.3 (72)
	10	1.1 (168)	2.0 (144)	2.2 (96)
	20	3.9 (168)	6.6 (96)	6.8 (72)
	40	26.0 (72)	21.0 (72)	20.7 (48)
Silanized fibre	5	0.6 (120)	1.0 (120)	1.3 (120)
	10	1.3 (144)	2.4 (144)	2.9 (120)
	20	3.8 (168)	6.4 (144)	6.7 (96)
	40	24.6 (144)	21.7 (144)	22.4 (120)

In the case of all fibre PP composites with a fibre content of 40%, the percentage of water absorption rapidly jumped at all absorption temperatures, which may have been due to the resulting porosity in the composites after processing with such a high fibre content, as presented in Fig. 3. This caused water to be more easily diffused in the composite.

Regarding the effect of the absorption temperature in the unmodified fibre PP composites, an increase in the absorbed water content as a function of the temperature can be observed for the lower fibre contents (5% and 10%). However, the increase of temperature from 50 °C to 70 °C was not significantly effective in increasing water uptake in the 20 wt% and 40 wt% fibre PP composites. This indicates that the water saturation capacity was not influenced by the absorption temperature in the presence of higher contents of fibre, meaning that the water absorption in the unmodified fibre PP composites was not governed by the diffusivity at a high temperature.



a) **b)**

Fig. 3. SEM micrographs of **a)** unmodified fibre PP composite (20 wt%) and **b)** unmodified fibre PP composite (40 wt%)

The data in Table 1 compare the percentage of water absorption and saturation time of the unmodified fibre composites with the modified fibre PP composites. It is clear that all of the fibre surface modifications were able to decrease the water uptake in the fibre PP composites due to substitution of hydroxyl groups with hydrophobic chemical moieties. All modified fibre PP composites showed good potential to considerably reduce the water absorption at equilibrium state, which indicated a lower capacity of water uptake. In addition, a general increase in the saturation time was observed for all of the modified fibre PP composites. The increase of saturation time together with the decrease of the water uptake capacity indicated lower velocity of water (*i.e.* lower mobility) in the composites. This means that the modified fibres in PP had a better ability to resist water uptake than the unmodified fibre, independently of the fibre content and absorption temperature. However, it appears that the water absorption at low fibre contents of 5 and 10 wt%, at 23 °C was significantly lower compared to the absorption at higher temperatures of 50 and 70 °C. This means that the capability of water absorption in EFBOP fibre/PP composites was strongly dependent on temperature of diffusion. The low mobility of water molecules at lower temperatures results in less diffusion into the composite material compared to the diffusion at higher temperatures.

Similarly to the unmodified fibre PP composites, the water absorption in modified fibre PP composites tended to increase with fibre percentage due to water-cellulose fibre interaction. Furthermore, the saturation time increased, maximized at 20 wt%, and then later decreased.

Compared with PPgMA modification techniques, the PPgMA-modified PP composite tended to have longer saturation and lower water absorption than that of the PPgMA blend composite. This means that grafting PPgMA on the surface of oil palm fibre could improve the water resistance better than the PPgMA blending method, which was probably a result of uniform distribution on the surface by PPgMA moieties, which act as a protective barrier.

Figure 4 presents the correlation between water absorption and fibre content at a temperature of 23 °C. The slope of the regression analysis is the ability of fibre content to absorb water, whereby unmodified fibre had the highest value and all modified fibre composites were lower. Compared with modified fibre composites, the silanized fibre composite had the lowest slope, which indicated the lowest ability to absorb water.

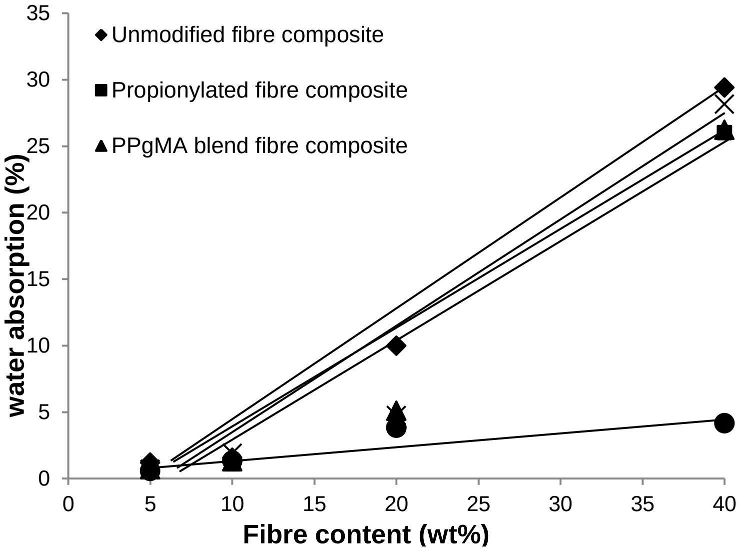


Fig. 4. The correlation of water absorption and fibre content at 23 °C

Figure 5 shows the fibre surface before and after modification.

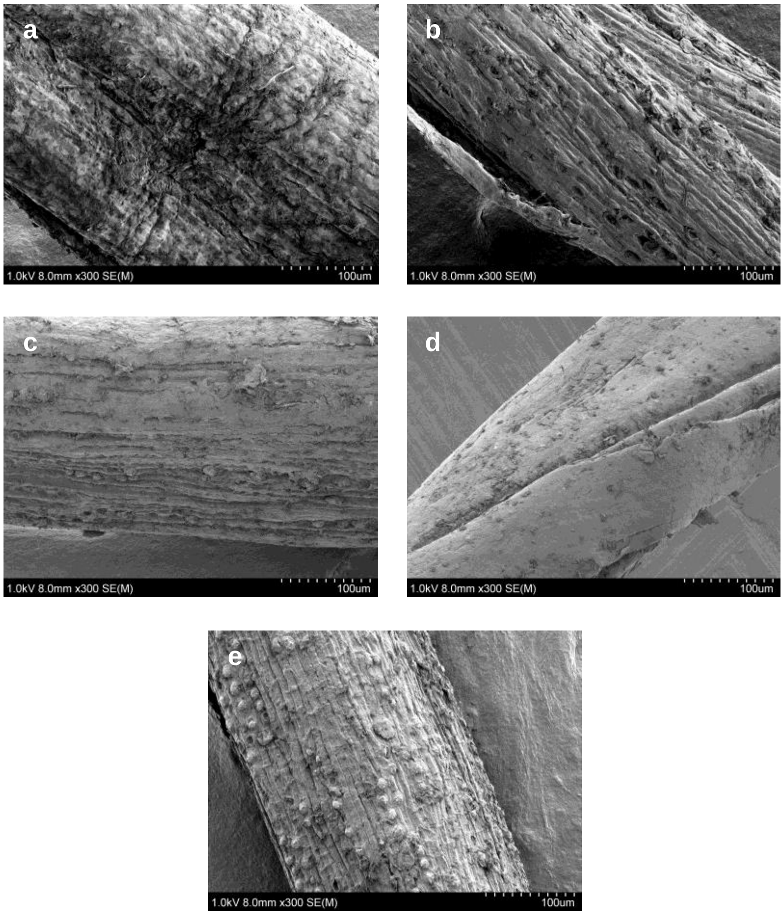


Fig. 5. SEM micrographs of EFBOP fibre a) before alkaline treatment, b) after alkaline treatment, c) after propionylation, d) after PPgMA modification, and e) after silanization

The micrographs confirmed that an alkaline treatment can remove wax and impurities from the fibre surface, giving a rough surface similar to what has been previously described (Alvarez *et al.* 2006). Such roughening should improve the adhesion and wettability with a PP matrix. The PPgMA-modified fibre presents PPgMA moieties grafted on the fibre, which was confirmed by FTIR in previous work (Kittikorn *et al.* 2012; Ndazi *et al.* 2007; Ndazi and Karlsson 2010).

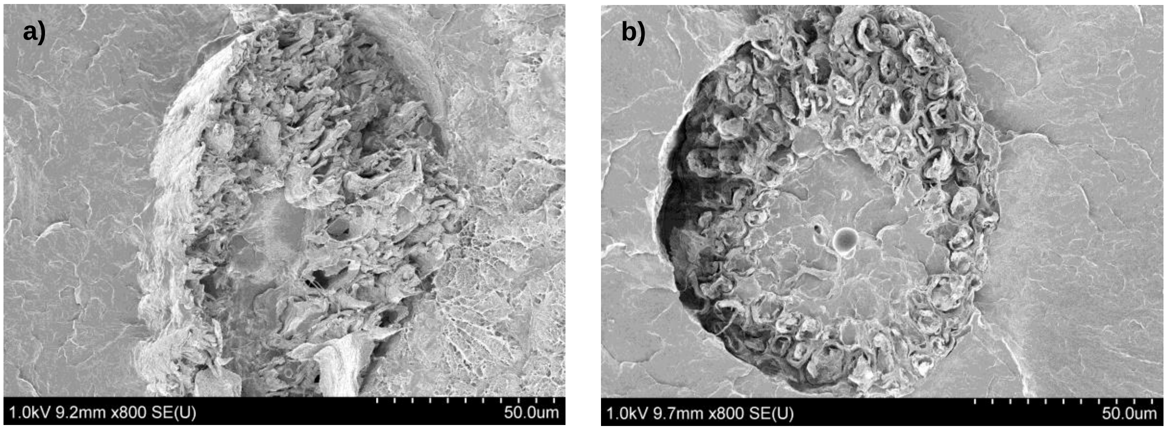


Fig. 6. SEM micrographs of fracture surface a) PPgMA-modified fibre PP composite and b) silanized fibre PP composite

Figure 6 presents fracture images of PPgMA-modified fibre and confirms what was stated above. The imbedded fibre in the matrix after fracture damage indicated good interfacial adhesion between the fibre and matrix, which influenced the improvement of mechanical properties considerably. As a previous work presented (Kittikorn *et al.* 2012), the modified fibre PP composites showed remarkably better tensile and fracture properties due to the enhancement of interfacial adhesion.

Sorption phenomena in fibre PP composites

The sorption of water in EFBOP fibre PP composites and prediction of diffusion mechanisms were studied by the use of Fick’s law. Table 2 summarizes the *n* and *k* values of each biocomposite at various temperatures. The unmodified fibre composite showed an *n* value close to 0.5 at 23 °C, regardless of the fibre content. This indicated that the diffusion of those biocomposites at this temperature occurred according to the Fickian model. When the temperature was increased, all modified fibre composites showed a diffusion behaviour approaching the Fickian model, as revealed by the *n* value being close to 0.5. This means that the amount of water absorption in the materials tended to linearly increase with the square root of time and gradually approach the equilibrium state. However, at an ambient temperature of 23 °C, all modified fibre composites had a lower *n* value, deviating noticeably from Fickian behaviour. Meanwhile, the value of the silanized fibre composite was the lowest of all modified fibres, which was due to the silane-coated surface barrier.

The *k* value is indicative of the interaction between water and materials. In the case of the unmodified fibre composite, the *k* value tended to continuously increase with increasing temperature. For modified fibre composites, the *k* values decreased or remained the same with increasing temperature, again showing that the unmodified composites had a greater interaction with the water.

Table 2. Correlation of Fibre Content to Temperature with regard to *n* and *k* Values

PP biocomposites	Fiber content (wt %)	23 °C		50 °C		70 °C	
		n	k(hr^2)	n	k(hr^2)	n	k(hr^2)
Unmodified fibre	5	0.54	0.15	0.38	0.27	0.21	0.37
	10	0.41	0.22	0.46	0.16	0.25	0.35
	20	0.36	0.16	0.44	0.18	0.33	0.28
	40	0.51	0.24	0.39	0.46	0.27	0.62
PPgMA blend fibre	5	0.25	0.35	0.29	0.31	0.49	0.13
	10	0.20	0.39	0.29	0.23	0.49	0.12
	20	0.30	0.23	0.49	0.11	0.48	0.12
	40	0.24	0.41	0.50	0.28	0.21	0.64
PPgMA modified fibre	5	0.19	0.37	0.28	0.25	0.31	0.35
	10	0.19	0.38	0.39	0.21	0.31	0.31
	20	0.25	0.28	0.48	0.13	0.53	0.23
	40	0.34	0.32	0.50	0.5	0.30	0.50
Propionylated fibre	5	0.33	0.19	0.35	0.2	0.36	0.22
	10	0.39	0.15	0.42	0.16	0.46	0.23
	20	0.44	0.10	0.47	0.14	0.49	0.16
	40	0.38	0.29	0.40	0.36	0.15	0.77
Silanized fibre	5	0.22	0.31	0.26	0.24	0.26	0.28
	10	0.23	0.30	0.36	0.13	0.45	0.21
	20	0.23	0.30	0.41	0.13	0.42	0.19
	40	0.22	0.32	0.42	0.11	0.38	0.34

Figure 7 presents the correlation between immersion time of the sample and M_t/M_∞ of the unmodified fibre composite at 23 °C. As previously presented, an increase of fibre content was remarkably effective in inducing water uptake to rapidly absorb, as observed by the time to equilibrium.

Table 3 shows the effect of fibre content and temperature on diffusion, sorption, and permeation of unmodified composites. It is apparent that the diffusivity of the composites increased markedly with an increase of temperature. This could be explained by the fact that the increased temperature increased the mobility of water molecules to diffuse into the composites. The relation between temperature and diffusion rate of surface-modified EFBOP fibre composite was regular, which indicated a distinctive mechanism of water absorption (Sreekala *et al.* 2002). Sorption of unmodified fibre composites also depended on temperature and fibre content. Because sorption is defined as the absorption ability of water into materials, the increased temperature would increase the mobility of water to absorb in the material.

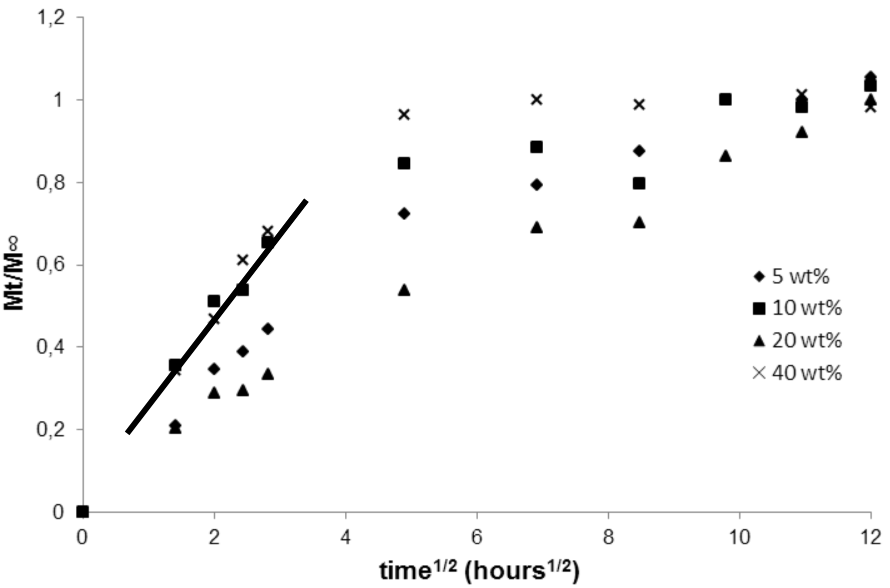


Fig. 7. The correlation between immersion time (hour^{½}) and M_t/M_∞ of unmodified fibre composite at 23 °C

As presented in Fig. 7, the absorption of water tended to proportionally increase with fibre content where voids in the composites were occupied by water, due to water-cellulose affinity. Permeation is defined as the penetration of water through a material, absorbed as calculated from the equation $P = D \times S$. The permeation of water into composites was dependent on temperature and fibre content. As can be seen from the data presented in Table 3, permeability continuously increased with temperature and fibre content for all formulations. Figure 8 presents the effect of surface modification on water uptake behaviour. It shows that all modified fibre composites reached equilibrium state slower than the unmodified fibre composite. This is a result of the increased moisture tolerance due to improved hydrophobic cellulose and enhancement of interfacial adhesion after surface modification.

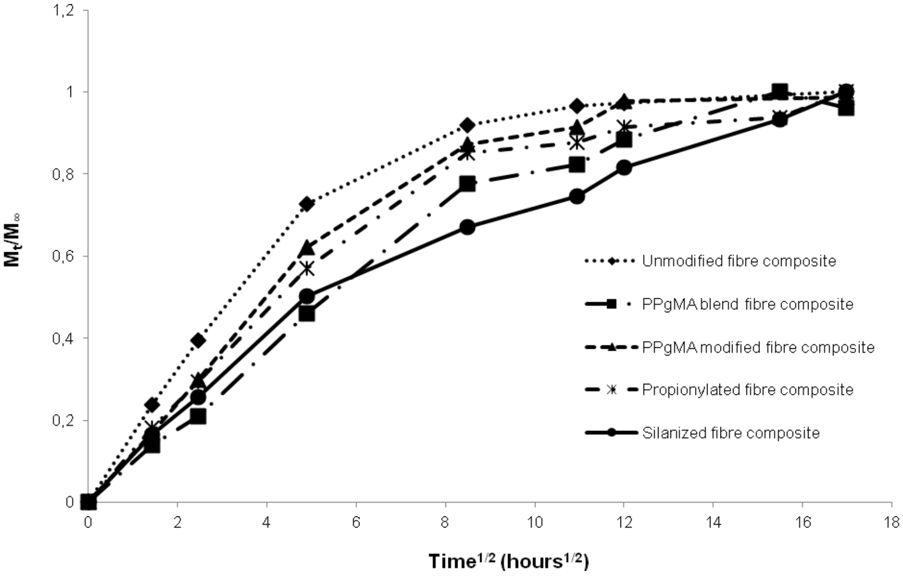


Fig. 8. The correlation between immersion time (hour^{½}) and Mt/Minf of all fibre composites for 20 wt% at 50 °C

Table 3. Diffusion, Sorption, and Permeation of Modified Fibre PP Composites

Biocomposites	temperature, °C	Fibre content wt%	Diffusitivity, m^2/s x 10^{-12}	Soption coefficient (g/g)	Permeability, m^2/s x 10^{-13}
Unmodified fibre	23	5	5.26	0.01	0.62
		10	7.06	0.02	1.11
		20	2.77	0.10	2.77
		40	18.73	0.29	55.07
	50	5	10.44	0.01	1.50
		10	11.00	0.02	2.69
		20	6.73	0.15	9.76
		40	51.97	0.26	133.23
	70	5	19.13	0.02	2.93
		10	20.54	0.03	6.23
		20	13.84	0.13	18.19
		40	73.77	0.29	211.56
PPgMA blend fibre	23	5	8.16	0.01	0.57
		10	15.43	0.01	2.04
		20	7.54	0.05	3.85
		40	28.91	0.26	75.83
	50	5	3.17	0.01	0.41
		10	7.57	0.03	2.01
		20	3.76	0.06	2.38
		40	20.34	0.23	47.63
	70	5	3.00	0.01	0.37
		10	5.55	0.03	1.89
		20	5.98	0.10	5.81
		40	71.11	0.27	193.58
PPgMA modified fibre	23	5	11.78	0.01	0.81
		10	12.79	0.02	2.47
		20	8.78	0.05	4.16
		40	33.99	0.28	95.74
	50	5	5.77	0.01	0.53
		10	6.21	0.03	1.65
		20	3.94	0.07	2.73
		40	29.38	0.23	66.48
	70	5	5.11	0.01	0.61
		10	9.80	0.03	3.23
		20	8.26	0.07	5.55
		40	51.55	0.23	116.80
Propionylated fibre	23	5	2.17	0.01	0.15
		10	2.49	0.01	0.28
		20	1.95	0.04	0.77
		40	22.06	0.26	57.38
	50	5	4.95	0.01	0.59
		10	3.15	0.02	0.62
		20	4.75	0.07	3.12
		40	40.11	0.21	84.38
	70	5	6.26	0.01	0.79
		10	9.80	0.02	2.16
		20	5.73	0.07	3.89
		40	84.23	0.21	174.37
Silanized fibre	23	5	9.00	0.01	0.52
		10	7.03	0.01	0.95
		20	8.57	0.04	3.27
		40	15.27	0.04	6.35
	50	5	4.62	0.01	0.44
		10	2.30	0.02	0.56
		20	2.67	0.06	1.70
		40	11.19	0.22	24.34
	70	5	7.69	0.01	0.97
		10	7.29	0.03	2.11
		20	6.79	0.07	4.51
		40	27.49	0.22	61.67

It was observed that the increase of temperature, besides increased fibre content, could noticeably increase the sorption coefficient. The value of sorption coefficients reached a maximum at 70 °C. The increased temperature increased the mobility of the water molecules, which in turn increased the penetration and absorption into the materials. Similarly, the diffusion coefficient of the modified fibre composites increased with temperature. However, at the low temperature of 23 °C, the modifications of the fibre by PPgMA blending, PPgMA modification, and vinyltrimethoxy silanization had a higher diffusion coefficient than that of the unmodified fibre composite. This could result from the presence of microvoids after the alkaline treatment, in which waxy material was extracted from the fibre surface, as demonstrated in Fig. 3b. The voids on the surface could promote the introduction of water molecules to diffuse through fibre rapidly due to capillary force. Nevertheless, at 23 °C, the sorption coefficient of all modified fibre composites was much lower than unmodified fibre composite. This indicated that absorbed water molecules in the fibres decreased due to the improved hydrophobicity of the modified fibres. Moreover, at high temperatures of 50 °C and 70 °C, the diffusion coefficient of all modified fibre composites was considerably lower than the unmodified composite. This can be explained by the fact that the modified fibre was still more effective in preventing the penetration of water molecules into the composites even at high temperatures, which resulted from better adhesion at the interface between the fibre and matrix phase.

Table 3 shows that the diffusion coefficient of unmodified fibre composites tended to increase with increasing temperature. This is similar to the results of previous work where the water diffusion in lignocellulosic fibres/PP composite was considerably affected by temperature variation (Espert *et al.* 2004). Among the modified fibre composites, the propionylated fibre composites had a lower diffusion coefficient compared to unmodified fibre composites, and it increased with temperature. However, in the PPgMA blend, PPgMA-modified, and silanized fibre PP composites, it was found that the diffusion coefficient decreased considerably at temperatures up to 50 °C, after which an increase was noted at a temperature of 70 °C. This phenomenon is due to changes in the material structure, which affected water diffusion, similar to previously reported research (Sreekala and Thomas 2003). The cited work showed that the water diffusion in modified fibres was decreased as the temperature was increased up to 50 ^{o}C and then turned up to increase with temperature increasing. At 23 °C, the modified fibre composites showed a similar diffusion coefficient to the unmodified fibre composite, but at 50 °C, the diffusion coefficients of the modified fibre composites were significantly lower than that of the unmodified composite. Thus, in comparison with unmodified fibres, the modified fibres in the biocomposite had the ability to protect against water penetration due to the grafting of the fibres. At 70 °C, the diffusion coefficient increased again, due to increased diffusion through the PP matrix due to higher mobility of water.

According to an earlier study of the water sorption behaviour of oil palm fibres with various types of surface modifications (Sreekala and Thomas 2003), it was found that at a low temperature of 30 °C, modified oil palm fibre had a maximum water uptake due to amorphous waxy materials positioned on the oil palm fibre surface that could trap water. However, when the temperature was increased, those waxy materials were removed, which resulted in a decrease in water absorption and a lower diffusion coefficient. The removal of waxy materials on the fibre surface by NaOH treatment promoted formation of voids in fibres, which simply facilitated water diffusion. Biocomposites with fibres modified by propionylation, PPgMA modification, silanization, and PPgMA blended all showed good water resistance due to enhanced hydrophobicity. It was, however, interesting to observe that using PPgMA as a compatibilizer in the melting process could result in similar performance in water without surface modification. Thus, it was demonstrated that using PPgMA in the melting process adequately improves the hydrophobic property without the need for chemical surface grafting.

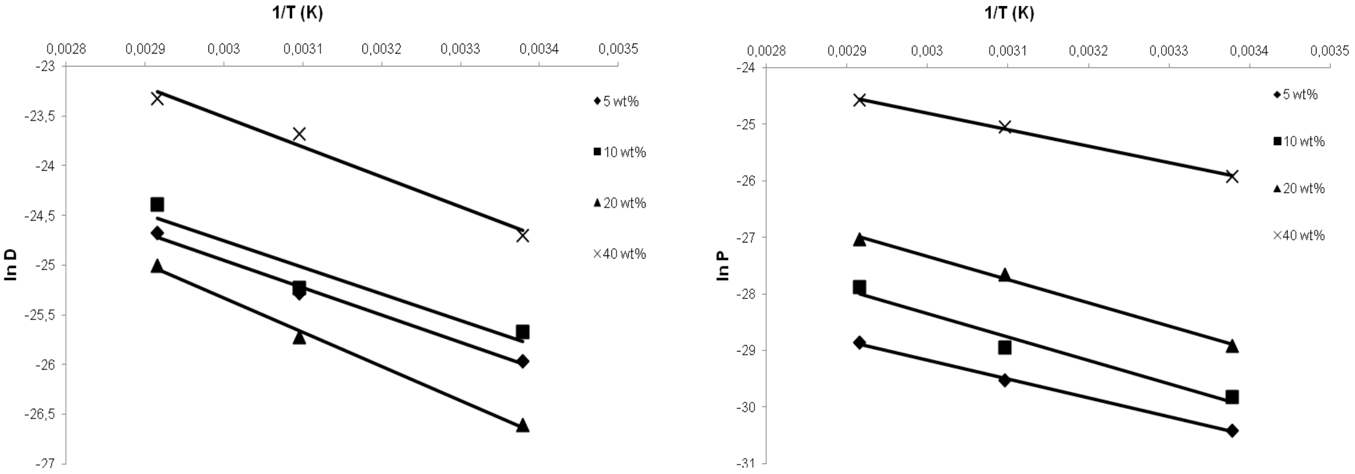


Fig. 9. Arrhenius plot between ln D and ln P *versus* 1/T of unmodified fibre composites

The Arrhenius plot demonstrates that the diffusion coefficient of unmodified and propionylated fibre composites was a linear function of temperature. This can be explained by the fact that the diffusion and permeation processes in the composite were dependent on temperature. A linear plot as a function of temperature was observed for unmodified fiber and propionylated fibre composites. This indicated that the diffusion of water was dependent on temperature and there was no phase changing.

Table 4. E_a and E_p of Unmodified Fibre Composites at Various Fibre Contents

Composite	Fibre content wt%	E_a, kJ mol^{-1}	E_p, kJ mol^{-1}
Unmodified fibre	5	23	28
	10	22	34
	20	29	34
	40	25	24
Propionylated fibre	5	24	31
	10	23	36
	20	26	30
	40	34	33

Table 4 presents the comparison of the activation energy of diffusion (E_a) and permeation (E_p) of unmodified and propionylated fibres PP composites. E_a and E_p were calculated from $\ln D = \ln D_0 - \frac{E_a}{RT}$ and $\ln P = \ln P_0 - \frac{E_p}{RT}$ by the Arrhenius plot between 1/*T* *versus* ln*D* and ln*P*, as presented in Fig. 9. It can be seen from Table 4 that E_a of the propionylated fibre composite tended to be significantly higher than E_a of the unmodified fibre composite. Basically, E_a indicates the activation energy of a diffused molecule required to reach equilibrium state in a material. The higher the E_a, the more resistance to water diffusion in the composite due to more water resistance ability of propionylated fibre.

Table 5. E_a and E_p of all Types of Fibre Composites

Composite	Fibre content wt%	E_a, kJ mol^{-1}	E_p, kJ mol^{-1}
Unmodified fibre	20	29	34
PPgMA blend fibre	20	21	41
PPgMA modified fibre	20	34	33
Propionylated fibre	20	26	30
Silanized fibre	20	43	45

The highest E_a and E_p values of the silanized fibre composite, compared to the other samples, indicated that the silanization of the fibres increased the resistance towards water molecules penetrating into the composite. Consequently, the most energy was required to approach the equilibrium state. This was attributed to low water-fibre affinity in the composite.

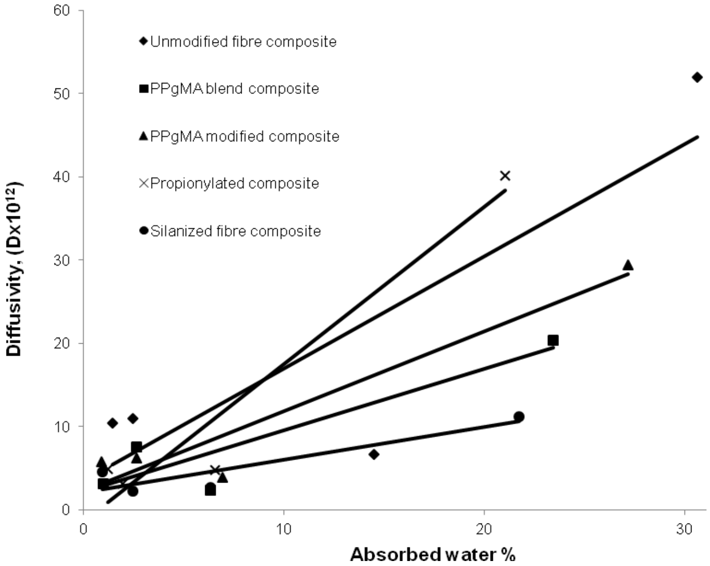


Fig. 10. Correlation between diffusion and absorbed water content at 50 °C

Figure 10 shows the correlation between diffusion and absorbed water content at 50 °C. The water resistance of modified fibre composites was higher than for composites containing unmodified fibres. It is shown that an initial increase of absorbed water would result in a reduction in the rate of water diffusion for all PP biocomposites. However, the rate of diffusion increased again at a high percentage of water absorption because of the high fibre content in the composites. At 40% fibre content, the PP matrix became more discontinuous and had a lower volume fraction, which allowed the water molecules to diffuse more easily through the plastic phase, reaching the fibre phase and resulting in the absorption of more water.

CONCLUSIONS

1. Decreased water absorption was obtained by chemical modification of fibres before manufacturing of biocomposites. The chemical substitution with hydrophobic compounds on hydroxyl groups of biofibres enhanced the interfacial adhesion between the fibres and the matrix and consequently reduced the water absorption in the biocomposites.
2. Surface morphology micrographs demonstrated increased surface roughness after alkaline treatments due to the extraction of wax or impurities from the surface.
3. Unlike PPgMA blending in the melting process, PPgMA modification resulted in fibre surfaces coated with PPgMA.
4. The degree of water absorption in biocomposites was found to be a function of fibre content and temperature. In general, all types of modifications resulted in PP biocomposites with lower water uptake in comparison with the unmodified fibres, even at high temperatures.
5. The vinyltrimethoxysilanized fibre composite exhibited superior water resistance, which was likely due to a barrier film covering the biofibres. At the same time, the PPgMA melt blend technique was a good method for manufacturing biocomposites with increased water resistance, with similar water diffusion to the PPgMA-modified solution.

ACKNOWLEDGMENTS

The financial support given by the Prince of Songkla University and KTH is gratefully acknowledged. The authors also thank Dr. Rosana Moriana Torro for her contribution in reviewing the manuscript.

REFERENCES CITED

Abdelmouleha, M., Boufia, S., Belgacemb, A., Duartec, A. P., Ben Salaha, A., and Gandini, A. (2004). "Modification of cellulosic fibres with functionalised silanes: Development of surface properties," *Int. J. Adhes. Adhes*. 24(1), 43-54.

Alvarez, V., Rodriguez, E., and Vazquez, A. (2006). "Thermal degradation and decomposition of jute/vinylester composites," *J. Therm. Anal. Calorim*. 85(2), 383-387.

Bledzki, A. K., and Gassan, J. (1999). "Composites reinforced with cellulose based fibers," *Prog. Polym. Sci*. 24, 221-274.

Espert, A., Camacho, W., and Karlsson, S. (2003) "Thermal and thermomechanical properties of biocomposites made from modified recycled cellulose and recycled polypropylene," *J. Appl. Polym. Sci*. 89(9), 2353-2360.

Espert, A., Vilaplana, F., and Karlsson, S. (2004). "Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties," *Comp. Part A* 35(11), 1267-1276.

González-Sánchez, C., González-Quesada, M., de la Orden, M. U., and Urreaga, J. M. (2008). "Comparison of the effects of polyethylenimine and maleated polypropylene coupling agents on the properties of cellulose-reinforced polypropylene composites," *J. Appl. Polym. Sci.* 110(5), 2555-2562.

Hill, C. A. S. (2006). "The use of timber in twenty-first century," *Wood Modification: Chemical, Thermal and Other Processes*, Wiley-VCH, Weinheim, Germany, 1-17.

Kittikorn, T., Strömberg, E., and Karlsson, S. (2012). "The effect of surface modifications on the mechanical and thermal properties of empty fruit bunch oil palm fibre PP biocomposites," *Polymer Renew. Resour.* 3(3), 79-100.

Kobiki, A., and Kawada, H. (2005). "Effect of water absorption on interaction between matrix cracking and fiber bridging for stress corrosion cracking of PMC," *JSME Int. J.* 48(4), 183-188.

La Mantia, F. P., and Morreale, M. (2011). "Green composites: A brief review," *Comp. Part A* 42(6), 579-588.

Law, K. N., Wan Daud, W. S., and Ghazali, A. (2007). "Morphological and chemical nature of fiber strands of oil palm empty-fruit-bunch (OPEFB)," *BioResources* 2(3), 351-362.

Najafi, S. K., Tajvidi, M., and Hamidina, E. (2007) "Effect of temperature, plastic type and virginity on the water uptake of sawdust/plastic composites," *Holz Roh Werkst.* 65 (5), 377-382.

Ndazi, B., Karlsson, S., and Nyahumwa, C. W. (2007). "Chemical and physical modifications of rice husks for use as composite panels," *Comp. Part A* 38(3), 925-935.

Ndazi, B., and Karlsson, S. (2010). "Characterization of the potential of soda cooking to extract fibrous residues from rice hulls," *Polymers from Renewable Resources* 3, 143-160.

Rozman, H. D., Peng, G. B., and Ishak Mohd, Z. A. (1998). "The effect of compounding techniques on the mechanical properties of oil palm empty fruit bunch–polypropylene composites," *J. Appl. Polym. Sci*. 70(13), 2647-1655.

Shinoj, S., Visvanathan, R., Panigrahi, S., and Kochubabu, M. (2011). "Oil palm fiber (OPF) and its composites: A review," *Ind. Crop. Prod*. 33(1), 7-22.

Sreekala, M. S., Kumaran, M. G., and Thomas, S. (1997). "Oil palm fibers: Morphology, chemical composition, surface modification, and mechanical properties," *J. Appl. Polym. Sci.* 66(5), 821-835.

Sreekala, M. S., Kumaran, M. G., and Thomas, S. (2002). "Water sorption in oil palm fiber reinforced phenol formaldehyde composites," *Comp. Part A* 33(6), 763-777.

Sreekala, M. S., and Thomas, S. (2003). "Effect of fibre surface modification on water-sorption characteristics of oil palm fibers," *Comp. Sci. Technol*. 63(6), 861-869.

Sreekumar, P. A., Thomas, S. P., Saiter, J. M., Joseph, K., Unnikrishnan, G., and Thomas, S. (2009). "Effect of fiber surface modification on the mechanical and water absorption characteristics of sisal/polyester composites fabricated by resin transfer molding," *Comp. Part A* 40(11), 1777-1784.

Strömberg, E., and Karlsson, S. (2009). "The effect of biodegradation on surface and bulk property changes of polypropylene, recycled polypropylene and polylactide biocomposites," *Int. Biodeterior. Biodegrad.* 63(8), 1045-1053.

Summerscales, J., Dissanayake, N. P. J., Virk, A. S., and Hall, W. (2010). "A review of bast fibres and their composites. Part 2 – Composites," *Comp. Part A* 41(10), 1336-1344.

Tserki, V., Zafeiropoulos, N. E., Simon, F., and Panayiotou, C. (2005). "A study of the effect of acetylation and propionylation surface treatments on natural fibers," *Comp. Part A* 36(8), 1110-1118.

Vilaplana, F., Strömberg, E., and Karlsson, S. (2010). "Environmental and resource aspects of sustainable biocomposites," *Polym. Degrad. Stab.* 95(11), 2147-2161.

Xie, Y., Hill, C. A. S., Xiao, Z., Militz, H., and Mai, C. (2010). "Silane coupling agents used for natural fiber/polymer composites: A review," *Comp. Part A* 41(7), 806-819.

Article submitted: December 7, 2012; Peer review completed: February 10, 2013; Revised version received and accepted: April 23, 2013; Published: April 30, 2013.